ULTRAVIOLET ABSORPTION SPECTRA OF SOLUTIONS OF PYRIDINE IN DIFFERENT SOLVENTS AND AT DIFFERENT TEMPERATURES

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ABSTRACT. The ultraviolet absorption spectra of solutions of pyridine in cyclohexane, 3-methyl pentane, carbon tetrachloride and isobutyl alcohol have been studied and the results have been compared with those for the vapour reported by previous workers. The two systems of bands due respectively to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are observed in the spectra due to solutions in cyclohexane, 3-methyl pentane and carbon tetrachloride, but the first system is totally absent in the spectrum of the solution in isobutyl alcohol. The interval between the successive bands in the first system is 542 cm^{-1}, which agrees closely with that observed in the case of the vapour. It has further been observed that the 0, 0 band in the first system shifts by about 430 cm^{-1} when pyridine is dissolved in the first three solvents. It is pointed out that these results confirm the explanation put forward by previous workers for the absence of the first system of bands in the case of the solution in alcohol. The $n \rightarrow \pi^*$ transition does not occur in this case because a bond is formed between the pyridine molecule and the alcohol molecule through the non-bonding electron of the nitrogen atom, but no such bond formation takes place in the solutions in the other solvents.

INTRODUCTION

From theoretical considerations Kasha (1950) suggested the probabilities of two types of electronic transitions in the pyridine molecule, one due to the excitation of one nitrogen non-bonding electron to π molecular orbital being designated as $n \rightarrow \pi^*$ transition and the other a singlet-singlet $\pi \rightarrow \pi^*$ transition. On scrutinising the absorption spectrum of pyridine vapour reported by Sponer and Stücklen (1946), the existence of two systems of bands due to the transitions mentioned above was confirmed by Rush and Sponer (1952). The 0, 0 band due to $n \rightarrow \pi^*$ transition (called the 1st system) is at 34769 cm^{-1} and that due to $\pi \rightarrow \pi^*$ transition (called the 2nd system) at 38350 cm^{-1}.

The absorption spectra of solutions of pyridine were studied by Herington (1950) who measured the molecular dissociation constant but did not observe the 1st system of bands. Stephenson (1954) also studied the absorption spectrum of solutions of pyridine in iso-octane and alcohol. From a comparison of the two absorption curves he concluded that the 1st system of bands was present in

the case of the iso-octane solution and it was absent in the spectrum due to the solution in alcohol.

Recently, Banerjee (1956) studied the ultraviolet absorption spectrum of pyridine in the liquid state and in the solid state at −180°C and found the first system of bands to be absent in both cases. He concluded that in the liquid and solid states, the pyridine molecule is attached to the neighbouring molecule through a new bond formed between non-bonding electron of the nitrogen atom and the hydrogen atom of the neighbouring molecule and therefore, the $n \rightarrow \pi^*$ transition does not occur.

The object of the present investigation was to study more exhaustively the influence of different environments and of temperature on both the systems of absorption bands of pyridine and to find out whether such bond formation is actually responsible for the disappearance of the first system of bands.

EXPERIMENTAL

The experimental arrangement was similar to that described in an earlier paper (Roy, 1956). Chemically pure pyridine from E. Merck was first fractionated and the proper fraction was redistilled under reduced pressure before use. The solvents used were cyclohexane, isobutyl alcohol, 3-methyl pentane and carbon tetrachloride. The solvents were found to have no absorption band in the region under consideration. The thicknesses of the two cells used were 5 mm and 3 cm. respectively and the strength of the solutions varied from .01% to .06% by weight. The spectra were photographed on Ilford HP3 films with a Hilger medium quartz spectrograph Iron arc spectrum was taken on each film as a comparison. Microphotometric records were taken with a Kipp and Zonen type self-recording microphotometer. The absorption spectra were calibrated with the help of the microphotometric records of iron lines using the method described in an earlier paper (Roy, 1956).

RESULTS

The microphotometric records of the absorption spectra of solutions of pyridine of different strengths in cyclohexane are given in figure 1 and those due to solutions in 3-methyl pentane, isobutyl alcohol and carbon tetrachloride are reproduced in figures 2 and 3. The frequencies of the absorption bands and probable assignemnts are given in Tables I, II and III. The data for the substance in the gaseous state reported by Rush and Sponer (1952) are also included in Table I for comparison.

DISCUSSION

It can be seen from figures 1(b) and 1(c) that the spectrum due to .06% solution in cyclohexane, with a cell thickness of 5 mm is identical with that

due to a thickness of 3 cm of .01% solution and there are three bands in the region, 35200 cm^{-1}—36284 cm^{-1}. The spectrum due to .01% solution of thickness

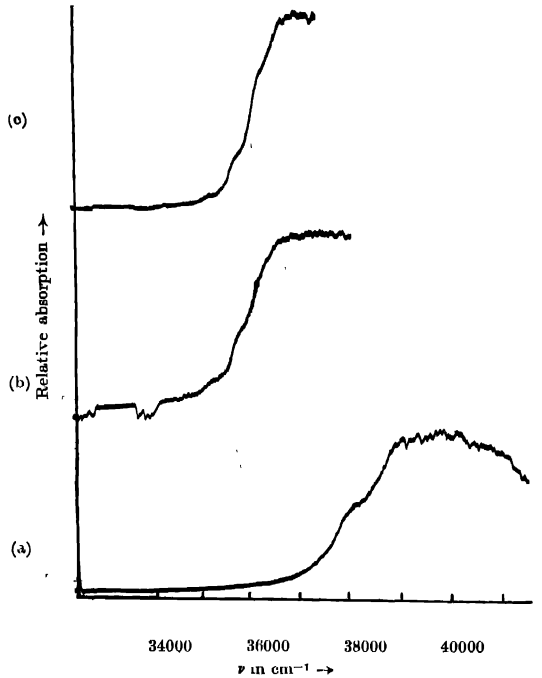

Fig. 1. Microphotomatric records of ultraviolet absorption spectra of solutions of pyridine in cyclohexane.

(a) .01 % solution in cyclohexane with 5 mm cell at 30°C
(b) .06 % „ „ „ „ „ „ „ „
(c) .01 % „ „ „ „ 3 cm „ „ „

5 mm, however, does not show these bands but a second system of bands with the first band at 37924 cm^{-1} is observed. A thicker cell produces complete absorption in this region. Evidently, the solution yields two systems of absorption bands, the weaker one being due to $n \rightarrow \pi^*$ transition and the stronger one due to the $\pi \rightarrow \pi^*$ transition. The solution in 3-methyl pentane, also, shows these two systems as can be seen in figure 2. When the solution is frozen it becomes rigid glass and two extra bands appear on the shorter wavelength side in the

first system. The positions of the first three bands, however, remain unchanged when the solution is frozen and cooled to −180°C. This shows that

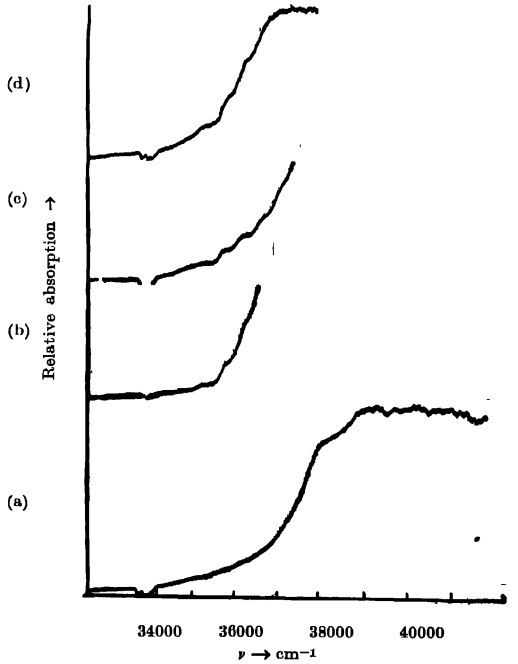

Fig. 2. Mycrophotometric records of ultraviolet absorption spectra of solutions of pyridine in 3-methyl pentane.

(a) .01% solution in 3-methyl pentane with 5mm cell at 30°C.
(b) .06% „ „ „ „ „ 5 mm „ „ 30°C.
(c) .06% „ „ „ „ „ 5 mm „ „ −180°C.
(d) .01% „ „ „ „ „ 3 cm „ „ 30°C.

first band is to be assigned to $0 \rightarrow 0$ transition in the system and not to $V \rightarrow 0$ transition. Figure 3 shows that in the spectra due to solution in isobutyl alcohol, the first system of bands is totally absent, there being full transmission in the region of these bands. These results thus corroborate the view put forward by Stephenson(1954) that the disappearance of the bands in the spectrum due to the solution in alcohol is due to the formation of a bond through the non-bonding electron of the nitrogen atom and OH group of the alcohol molecule. It is further proved by these results that such bond formation does not take place in the solutions in cyclohexane and 3-methyl pentane.

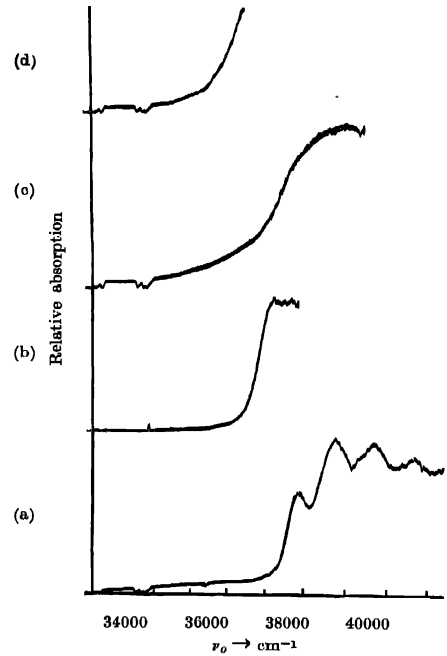

Fig. 3. Mycrophotometric records of ultraviolet absorption spectra of solutions of pyridine in different solvents.

(a) .01% solution in isobutyl alcohol with 5 mm cell at — 180°C.
(b) .06% „ „ „ 5 mm cell at — 180°C.
(c) .01% „ carbon tetrachloride with 5 mm cell at 30°C.
(d) .06% „ „ „ 5 mm cell at 30°C.

The 0, 0 band in the first system due to pyridine vapour is at 34769 cm^{-1} (Rush and Sponer, 1952), but in the solutions either in cyclohexane or in 3-methyl pentane the band of the first system is at 35200 cm^{-1}. Hence this band is shifted towards shorter wavelength by about 431 cm^{-1} by the influence of the solvents. These bands are also much wider than the corresponding bands due to vapour. This broadening is evidently due to the fluctuation of the intermolecular forces in the solution. The interval between successive bands is 542 cm^{-1} which agrees closely with those observed in the case of the vapour (Rush and Sponer, 1952).

The spectrum due to the solution in carbon tetrachloride (figure 3) does not show discrete bands in the first system, but the absorption curves rise as steeply as in the case of solution in 3-methyl pentane. Probably, the bands are

TABLE I

Absorption spectra of pyridine

Vapour (prominent bands) Rush & Sponer, 1952		.01% sol. in cyclohexane .5cm cell (liq.)		.01% sol. in cyclohexane 3cm cell (liq.)		.06% sol. in cyclohexane .5cm cell (liq.)	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
1st system		*1st system*		*1st system*		*1st system*	
34769	0, 0	No discrete band observed		35200	0, 0	35200	0, 0
35311	$0+542$			35742	$0+542$	35742	$0+542$
35633	$0+864$			36284	$0+542\times2$	36284	$0+542\times2$
35855	$0+542\times2$						
36397	$0+542\times3$						
2nd system		*2nd system*		*2nd system*		*2nd system*	
38350	0, 0	38070	0, 0	Total absorption		Total absorption	
		39020	$0+950$				
		39971	$0+950\times2$				
		40821	$0+950\times3$				

TABLE II

Absorption spectra of pyridine

.01% sol. in 3-methyl pentane .5cm cell (liq.)		.01% sol. in 3-methyl pentane 3cm cell (liq.)		.06% sol. in 3-methyl pentane .5cm cell (liq.)		.06% sol. in 3-methyl pentane (solid $-180°$C) .5cm cell	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
1st system		*1st system*		*1st system*		*1st system*	
No discrete band observed		35200	0, 0	35200	0, 0	35200	0, 0
		35742	$0+542$	35742	$0+542$	35742	$0+542$
		36286	$0+542\times2$	36286	$0+542\times2$	36286	$0+542\times2$
					—	36828	$0+542\times3$
						37370	$0+542\times4$
2nd system		*2nd system*		*2nd system*		*2nd system*	
38947	$0+950$	Total absorption		Total absorption		Total absorption	
39897	$0+950\times2$						
40847	$0+950\times3$						

TABLE III

Absorption spectra of pyridine

.01% sol. in isobutyl alcohol .5 cm cell		.06% sol. in isobutyl alcohol (solid −180°C) .5 cm cell		.01% sol. in carbon tetrachloride .5 cm cell		.06% sol. in carbon tetrachloride .5 cm cell	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
1st system Absent		*1st system* Absent		*1st system* Unresolved		*1st system* Unresolved	
2nd system		*2nd system*		*2nd system*		*2nd system*	
37924	0, 0			37924	0, 0		
38874	0+950	Total absorption		38874	0+950	Total absorption	
39828	0+950×2						
40776	0+950×3						

much broader in this case and they are not resolved from each other. The nature of the curve shows, however, that in this case also, the first system shifts as much towards shorter wavelengths as in the solution in 3-methyl pentane.

In the absorption spectrum of pyridine in the liquid state and in the solid state at −180°C, the first system is totally absent (Banerjee, 1956). This shows that the non-bonding electron of the nitrogen atom forms a bond with the hydrogen atom of the pyridine ring. Hence the nature of the hydrogen atom in the ring is different from that of the hydrogen atom in cyclohexane or 3-methyl pentane.

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